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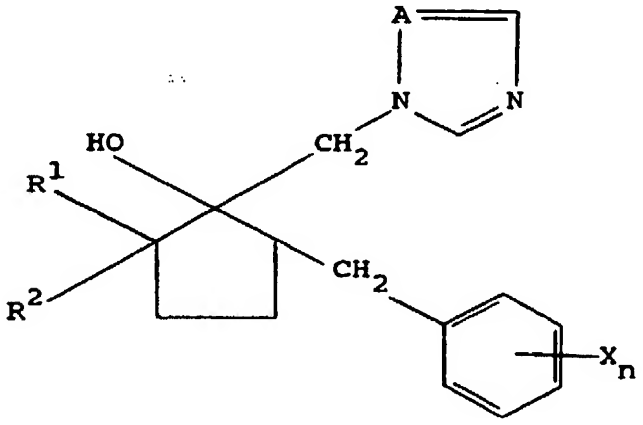
(54) Fungicidal compositions.

(57) A fungicidal composition which comprises a compound of general formula :



(I)

or acid addition salts or metal complexes thereof, wherein R^1 and R^2 each independently represents a C_{1-5} alkyl group or a hydrogen atom ; X represents a halogen atom, a C_{1-5} alkyl group or a phenyl group ; n is 0, 1 or 2 and A represents a nitrogen atom or CH ; and an aliphatic alcohol alkoxylate, for example an ethoxylate, with an average of 5-9 ethylene oxide units per molecule, of a C_{9-15} aliphatic alcohol, as adjuvant. It has been found that the presence of the alkoxylate substantially enhances the fungicidal efficacy of a compound of general formula I, in particular in foliar spray applications against fungi which are pathogenic to cereal crops.

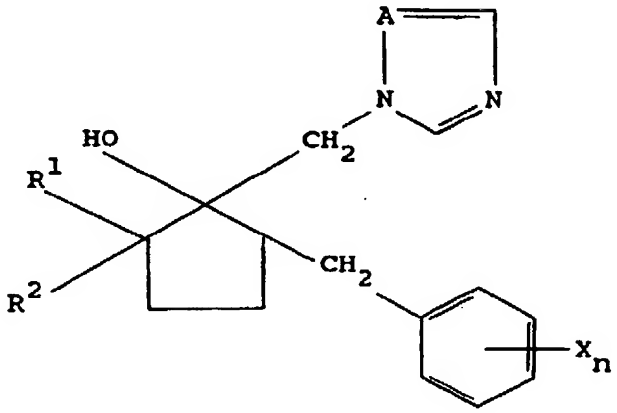
EP 0 526 206 A1

The invention relates to fungicidal compositions, to their use in combating undesired fungal organisms, and to their preparation.

The invention concerns,in particular, novel fungicidal compositions which incorporate benzyl triazolyl cyclopentane compounds as disclosed in GB-A-2180236 and EP-A-267778.

It has now been discovered that the fungicidal activity of the aforementioned compounds is enhanced to a surprising and significant extent by the co-application to a plant to be treated, of an adjuvant selected from a particular class, namely aliphatic alcohol alkoxylates. Testing has revealed that, whilst adjuvants of various classes cause some enhancement of activity, the enhancement of activity caused by aliphatic alcohol alkoxylates is particularly interesting. The aliphatic alcohol alkoxylates as a class appear, surprisingly, to stand apart from other adjuvants, providing very high enhancement of activity, consistently over a wide range of adjuvant and active ingredient application rates, whilst being substantially non-phytotoxic. Moreover, they are very suitable for the development of practical formulations.

In accordance with a first aspect of the present invention, there is provided a fungicidal composition which comprises a compound of general formula:



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or acid addition salts or metal complexes thereof, wherein R^1 and R^2 each independently represents a C_{1-5} alkyl group or a hydrogen atom; X represents a halogen atom, a C_{1-5} alkyl group or a phenyl group; n is 0, 1 or 2 and A represents a nitrogen atom or CH; and an alkoxylate of an aliphatic alcohol.

In accordance with a second aspect of the present invention, there is provided a method of combating a fungus at a locus, comprising treating the locus with a composition of the invention.

In the method according to the invention, the locus may be an agricultural or horticultural locus, for example, plants subject to fungal attack, seeds of such plants or the medium in which plants are growing or are to be grown. The method may comprise combating a fungus already present at a locus and/or prophylactic fungicidal treatment at a locus. Preferably, the method according to the invention involves the foliar treatment of plants with the composition. The composition may be used to control a large number of fungal diseases of plants. Reference is made to the list on pages 36 to 37 of EP 267778, which list in incorporated herein by reference. In particular, the plants may suitably be cereals, especially wheat or barley plants, because of the high level of control achieved by the method of the invention against infestations of the fungi Erysiphe graminis (powdery mildew) and Leptosphaeria nodorum (septoria).

Preferably, the method of the invention comprises treating the locus with an aqueous composition which comprises a compound of general formula I and an alkoxylate of an aliphatic alcohol.

A preferred alkoxylate of an aliphatic alcohol is based on alkoxy units having 2 carbon atoms, thus being an ethoxylate, or 2 and 3 carbon atoms, thus being a mixed ethoxylate/propoxylate. An ethoxylate is preferred. Such alcohol alkoxylates are available from various sources or may be prepared by alkoxylating a suitable aliphatic alcohol under known conditions.

In preferred aliphatic alcohol alkoxylates for use in the present invention, the alkoxylate chain may have at least 5 alkoxy moieties, suitably from 5 to 25 alkoxy moieties, preferably from 5 to 15, and most preferably from 5 to 9.

In preferred alcohol alkoxylates for use in the present invention, the alcohol moiety is derived from a C_{9-18} aliphatic alcohol, preferably a C_{9-15} aliphatic alcohol. As is well known, such alcohols are normally available in the form of mixtures. However, it may be stated that, in the context of the present invention, preferred

alcohols are primary or predominantly primary, straight chain or predominantly straight-chain, alcohols and with one hydroxy group or predominantly with one hydroxy group. They may be saturated or unsaturated but the highest activity has been shown by saturated alcohol alkoxylates, or alcohol alkoxylates in which saturated alcohol moieties predominate. The terms "predominate" and "predominantly" denote "more than 50% by weight" and, preferably, "at least 80% by weight".

Good results have been obtained using alcohol alkoxylates in which the alcohol is of vegetable or animal oil origin. Good results have also been obtained using alcohol alkoxylates in which the alcohol is of mineral oil origin.

In the method of the invention, the presence of an alkoxylate of an aliphatic alcohol may substantially reduce the quantity of a compound of general formula I which needs to be applied to a locus to obtain a given level of activity. In practice, a compound of general formula I may suitably be applied to a locus in an amount in the range of from 20 to 600 g/ha, preferably 50 to 300 g/ha. The adjuvant may suitably be applied to a locus in an amount in the range of from 80 to 2000 g/ha, preferably 300 to 1500 g/ha.

Whilst a composition comprising an aliphatic alcohol alkoxylate and a compound of general formula I may have other fungicidal indications, it is likely to be of primary benefit for therapeutic foliar applications. Activity can be enhanced or broadened by co-application of a further fungicidal compound, suitable examples being dithianon, chlorothalonil and fenpropimorph. Preliminary tests have indicated that the enhancement effect which the alkoxylate adjuvant has on a compound of general formula I remains, when such a compound is also applied. Such a compound, when co-applied, may suitably be co-applied in an amount in the range of from 20 to 1200 g/ha, preferably 100 to 800 g/ha.

It may be desirable to co-apply further compound(s) to a said locus, for example an insecticide, acaricide, herbicide or nematocide, or a fertilizer.

In accordance with a further aspect of the present invention, there is provided an aqueous composition for use in the method of the invention, to be applied to a said locus. Such a composition may be prepared by mixing an aliphatic alcohol ethoxylate and a composition containing a compound of general formula I, taken from separate sources, in water in a tank; or, preferably, by adding, to water in a tank, a pre-mixed "one-pack" formulation containing both an aliphatic alcohol alkoxylate and a compound of general formula I. Such a pre-mixed formulation may most conveniently be a liquid or a wettable powder, the manufacture of each of which is entirely standard.

An antifoaming agent may be employed, if desired, in accordance with standard practice. An antifoaming agent may be a constituent of a "one-pack" formulation. When the aqueous composition is to be prepared by mixing an aliphatic alcohol ethoxylate, and a composition containing a compound of general formula I in a tank, and an antifoaming agent is desired, the antifoaming agent may conveniently be formulated with the ethoxylate component.

Conventionally, antifoaming agents are selected on the basis of compatibility with the formulation to be prepared; thus, for example, solubility of the antifoamer in the formulation has to be checked. Selection on such a basis is entirely routine in formulation technology. It was expected that, if needed, for the compositions of the present invention, and especially for the "one-pack" formulations, compatible, conventional antifoaming agents, including silicone-based products, would be suitable. However, it has been found that conventional agents such as silicone-based products are in fact not suitable for use with the compositions of the present invention.

Surprisingly, it has now been found that certain paraffinic oils, which are not conventional antifoaming agents, are not only compatible with compositions of the present invention but also provide useful antifoaming properties, where needed. It is therefore preferred that the composition of the present invention is used in conjunction with a paraffinic oil as antifoaming agent, e.g. as an ingredient of the composition or by addition with the formulation ingredients when prepared in a tank mix with water.

Usually, paraffinic oils are derived from petroleum sources and are composed of paraffinic and aromatic, usually naphthenic, hydrocarbons. Suitable paraffinic oils for use as antifoaming agent with a composition of the present invention, have a molecular weight in the range of from 140 to 180 and contain in the range of from 45 to 100%, preferably 50 to 100% paraffinic hydrocarbons.

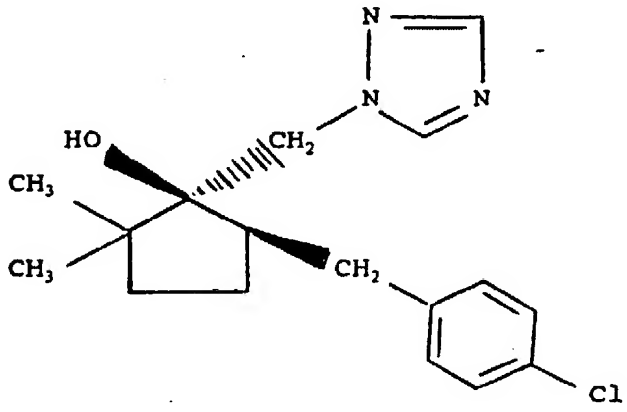
The concentration of the components in the aqueous composition may be calculated from the amount of a compound of general formula I and of alkoxylate it is desired to supply, and the rate of application of the composition (that is, the volume applied). Typically the rate of application of the composition may be in the range of from 100 to 1000 l/ha. Thus, when the rate of application of the composition is to be 1000 l/ha, and that of a compound of general formula I and of the alkoxylate, 100 g/ha and 400 g/ha, respectively, the aqueous composition will contain 0.1 g/l of a compound of general formula I and 0.4 g/l of alkoxylate. Generally, the aqueous composition may contain from 0.02 to 6.0 g/l of a compound of general formula I and from 0.08 to 20 g/l alkoxylate.

In accordance with a further aspect of the present invention, there is provided a concentrate formulation

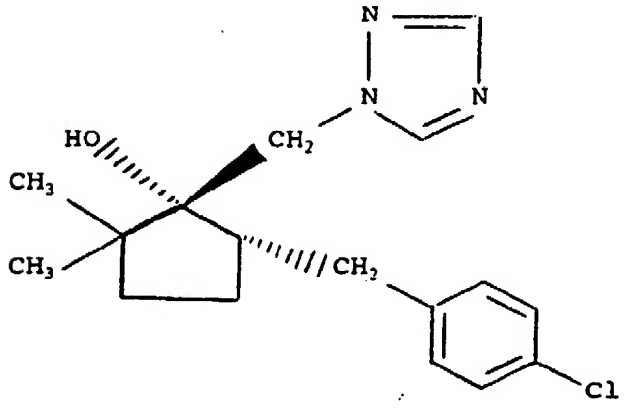
containing an alkoxylate of an aliphatic alcohol and of a compound of general formula I, for dispersion or dissolution in water. Such a concentrate formulation may suitably contain from 5 to 200 g/kg, preferably 30 to 120 g/kg, of a compound of general formula I and from 100 to 1000 g/kg, preferably 400 to 700 g/kg, of adjuvant, the balance of the concentrate formulation being the usual types of further materials. Useful formulations arise from a weight ratio of in the range of from 5:1 to 20:1, preferably from 5:1 to 10:1, of alkoxylate adjuvant to compound of general formula I.

With reference to compounds of general formula I, it will be appreciated that these will have optical isomers; three optical centres can be present, or two when R^1 and R^2 are identical. The method of the invention may employ a compound of general formula I in the form of a single isomer, or in the form of a racemic mixture, or in the form of any other mixture of optical isomers.

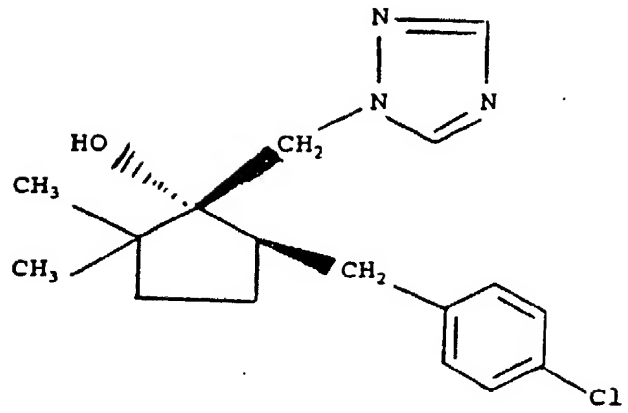
For example, when R^1 and R^2 are identical, the following isomers may be present:



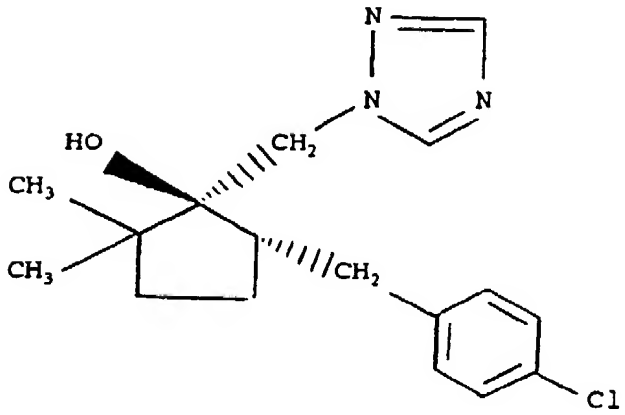
(Ia)



(Ib)



(Ic)



(Id)

Forms Ia and Ib are hereinafter referred to as the "cis" isomers. Forms Ic and Id are hereinafter referred to as the "trans" isomers. In using the terms "cis" and "trans", reference is thus being made to the relative positions of the hydroxy and halobenzyl groups.

Most preferably, a compound of general formula I is in the form of the "cis" isomers or a mixture of "cis" and "trans" isomers, in which "cis" isomers predominate. For the preparation thereof, reference is made to EP-A-357404 and EP-A-267778, respectively.

Preferably, R^1 in a compound of general formula I represents a hydrogen atom or a C_{1-4} alkyl group, and R^2 represents a hydrogen atom or a C_{1-4} alkyl group. Most preferably, each of R^1 and R^2 represents a methyl group.

Preferably, A in a compound of general formula I represents a nitrogen atom.

Preferably, X_n in a compound of general formula I represents a halogen atom at the 4-position of the benzene ring.

Preferably, X in a compound of general formula I represents a fluorine, chlorine or bromine atom, most preferably a chlorine atom. n preferably is 1.

The invention extends to a method for the preparation of a composition as described herein.

The invention will now be further described with reference to the accompanying Examples.

Example Set 1

a) Materials

The following emulsifiable concentrate (EC) and suspension concentrate (SC) formulations of a compound of general formula I were prepared, the EC by blending the components and the SC by blending and milling the components in a bead mill.

The active ingredient (a.i.) used for Trials 1-5, described hereafter, of Example Set 1, was an 80/20 mixture of the "cis" isomers and the "trans" isomers (i.e. thought to be a 40/40/10/10 mixture of form Ia, Ib, Ic and Id) of the compound 1-(4-chlorobenzyl)-3,3-dimethyl-2-hydroxy-2-(1,2,4-triazol-1-yl)methylcyclopentane (i.e. compound of general formula I wherein $R^1 = R^2 = CH_3$, X_n = 4-Cl, A = N).

The active ingredient (a.i.) used for Trials 6-7, described hereafter, of Example Set 1, was substantially the "cis" isomers, (thought to be a 50/50 mixture of forms Ia and Ib) of the same compound.

Emulsifiable concentrate		Suspension concentrate	
a.i.	100 g	a.i.	188 g
TENSIOFIX XN6	18 g	VANISPERSE	25 g
TENSIOFIX XN10	42 g	KELZAN	2.5 g
SURFADONE LP100	60 g	BEVALOID 642	1.0 g
N-butanol	40 g	PROXEL GXL	1.5 g
SHELLSOL A	to 1 l	propylene glycol	120 kg
		water (tap)	to 1 kg

TENSIOFIX surfactants are emulsifiers, from Omnichem Belgium.

SURFADONE LP100 is an n-octyl pyrrolidone solvent, from GAF Ltd.

SHELLSOL A is a solvent, trimethyl benzene, from Shell

VANISPERSE is a dispersant, a fractionated sodium salt of oxylignin, from Trafford Chemicals.

KELZAN is an industrial grade xanthan gum, from Merck & Co. or Kelco International.

BEVALOID 642 is an antifoaming agent, from Bevaloid Ltd.

PROXEL GXL is an aqueous dipropylene glycol solution of the preservative 1,2-benzisothiazolin-3-one, from ICI.

The following adjuvants were employed:

- GENAPOL C-050, C-080, C-100 and C-200 - alcohol ethoxylate adjuvants from Hoechst in which the alcohol moiety is derived from coconut oil, and the ethoxylate moiety has an average 5, 8, 10 or 20 ethylene oxide units per molecule, respectively.

Alcohols derived from coconut oil typically comprise the following components (ref. E. W. Eckey "Vegetable Fat & Oils", published by Reinhold Publishing Corp. 1954, N.Y.)

caprylic (C_8) - 9.0 %
capric (C_{10}) - 6.8 %
lauric (C_{12}) - 46.4 %
myristic (C_{14}) - 18.0 %
palmitic (C_{16}) - 9.0 %

- GENAPOL O series adjuvants, from Hoechst. Corresponding to GENAPOL C series but having oleyl/C_{16-18} unsaturated alcohol moieties.

- ATLAS G-1281 - a polyoxyethylene fatty glyceride, from ICI.
- ARKOPAL N-060, N-100 and N-230 - C_9 alkyl phenol adjuvants from Hoechst, in which the ethoxylate moiety has an average 6, 10 and 23 ethylene oxide units per molecule, respectively.
- HVI 60 - a paraffinic oil adjuvant containing 100 g/l EMULSOGEN M, a castor oil ethoxylate from Hoechst.
- DOBANOL alcohol ethoxylates, from Shell. The nomenclature of the DOBANOL ethoxylates is such that DOBANOL 91, 23, 25 and 45 ethoxylates have C_{9-11}, C_{12-13}, C_{12-15} and C_{14-15} primary alcohol moieties, whilst the number after the hyphen denotes the average number of ethoxy units per molecule.

b) Plants

Wheat plants (Triticum aestivum cv Hornet and cv Norman) were grown to the 2-3 leaf stage under normal glasshouse propagation conditions (top watering; temperature, 20-25°C; lighting, 16 h photoperiod of daylight supplemented by mercury vapour/sodium lamps).

The variety (cv Hornet) was inoculated with dry Erysiphe graminis fsp tritici (powdery mildew) from diseased plants 1 day before spraying and held under glasshouse conditions until sprayed. The variety (cv Norman) was inoculated with Leptosphaeria nodorum (septoria; glume blotch) using an aqueous suspension of spores washed from agar plates also 1 day before spraying. The inoculated plants were held at 21°C under high humidity conditions for 18 h. They were then brought to glasshouse conditions and allowed to dry before being sprayed.

c) Preparation and application of spray solutions

Two series of adjuvants were tested in two trials, each conducted in the same manner. Aliquots (1.25, 0.63, 0.32, 0.16, 0.08, 0 ml) of the EC formulation and amounts (1.33, 0.66, 0.33, 0.16, 0.08, 0 g) of the SC formulation were each dispersed in tap water (250 ml). Amounts (2.5 g) of each adjuvant were also dispersed in tap water (250 ml). An aliquot (20 ml) of each formulation dispersion was mixed with an equal aliquot of adjuvant solution to give arrays of dispersions for each formulation type.

These dispersions were sprayed onto pairs of pots of each variety of wheat plants at a volume rate of 400 l/ha. At this rate and at the concentrations used, the applications were equivalent to 100, 50, 25, 12.5, 6.3 and 0 g/ha of a.i. for the EC formulation and 200, 100, 50, 25, 12.5 and 0 g/ha of a.i. for the SC formulation. The application rate of adjuvant was equivalent to 1 kg/ha.

d) Assessment

The sprayed plants were allowed to dry and returned to the glasshouse conditions given above, except that the watering was by automated sub-irrigation. Assessment of disease was by visual assay at 6-8 days (powdery mildew) or 8-10 days (septoria) after spraying. For septoria the extent of infection was assessed on a scale 0-9 (0 = no infection, 9 = sporulating lesions and necrotic tissue completely covering inoculated foliage). The assessment for powdery mildew was on a 0-9 scale, as for septoria, or was an estimate of the % area covered by sporulating lesions on the inoculated foliage.

The 0-9 scale is referred to in the Results as the "Infection Score".

e) Results

A series of seven trials were carried out as described above and Tables 1 to 17 contain the mean results of the two independent assessments of the leaves inoculated and sprayed for each treatment.

It will be observed that, whilst all adjuvants tested gave some enhancement of activity of at least one combination of adjuvant application rate and active ingredient application rate, that the only adjuvants which gave good enhancement at all combinations tested were the GENAPOL and DOBANOL alcohol ethoxylates.

Trial 1 - Effect of adjuvants on the therapeutic control of 1 day old infections of powdery mildew on wheat

a) EC formulation. Table 1

ADJUVANT appln. rate 1 Kg/ha	% LEAF AREA SPORULATING LESIONS					
	a.i. application rate, g/ha					
	0	6.3	12.5	25	50	100
none	73	58	40	28	13	7
GENAPOL C-050	70	38	25	5	5	5
GENAPOL C-080	65	40	10	9	6	10
GENAPOL C-100	68	20	20	6	5	5
GENAPOL C-200	55	30	23	9	6	5

b) SC formulation. Table 2

ADJUVANT appln. rate 1 Kg/ha	% LEAF AREA SPORULATING LESIONS					
	a.i. application rate, g/ha					
	0	12.5	25	50	100	200
none	65	53	53	40	35	25
GENAPOL C-050	75	20	13	10	7	10
GENAPOL C-080	48	10	6	7	5	5
GENAPOL C-100	68	20	15	9	9	6
GENAPOL C-200	63	28	23	10	6	6

Trial 1 - Effect of adjuvants on the therapeutic control of 1 day old infections of septoria on wheat

a) EC formulation. Table 3

ADJUVANT appln. rate 1 Kg/ha	INFECTION SCORE a.i. application rate, g/ha					
	0	6.3	12.5	25	50	100
none	7.5	5	3.5	1.5	1	0
GENAPOL C-050	5.5	2	1	0	0	0
GENAPOL C-080	6	1.5	0.5	1	0.5	1
GENAPOL C-100	6	2	0.5	1	0.5	1.5
GENAPOL C-200	6.5	3	2.5	1.5	1	1

b) SC formulation. Table 4

ADJUVANT appln. rate 1 Kg/ha	INFECTION SCORE a.i. application rate, g/ha					
	0	12.5	25	50	100	200
none	4.5	3	2.5	2	2.5	1
GENAPOL C-050	4	1.5	0.5	0	0	0
GENAPOL C-080	3.5	0.5	1	0	0	0.5
GENAPOL C-100	5	1	1	0.5	0	1
GENAPOL C-200	6	2	0.5	0	0.5	0.5

Trial 2 - Effect of adjuvants on the therapeutic control of 1 day old infections of powdery mildew on wheat

a) EC formulation. Table 5

ADJUVANT appln. rate 1 Kg/ha	% LEAF AREA SPORULATING LESIONS a.i. application rate, g/ha					
	0	6.3	12.5	25	50	100
none	97.5	75	65	48	8	2
ARKOPAL N-060	78	50	23	8	5	0
ARKOPAL N-100	88	28	13	3	1	1
ARKOPAL N-230	90	33	20	10	4	1
emulsified paraffin oil	90	38	11	2	2	0

b) SC formulation. Table 6

ADJUVANT appln. rate 1 Kg/ha	% LEAF AREA SPORULATING LESIONS a.i. application rate, g/ha					
	0	12.5	25	50	100	200
none	90	80	68	65	45	55
ARKOPAL N-060	75	28	5	0	1	0
ARKOPAL N-100	83	20	4	2	1	1
ARKOPAL N-230	93	28	10	1	1	1
emulsified paraffin oil	93	9	3	1	0	0

Trial 2 - Effect of adjuvants on the therapeutic control of 1 day old infections of septoria on wheat

a) SC formulation. Table 7

ADJUVANT appln. rate 1 Kg/ha	INFECTION SCORE a.i. application rate, g/ha					
	0	6.3	12.5	25	50	100
none	8	7	6.5	5	1.5	0.5
ARKOPAL N-060	8.3	6	4	4.5	1.3	3
ARKOPAL N-100	8.5	5	2.8	3	2	3
ARKOPAL N-230	8	4.3	3.5	2.8	2.5	3.3
emulsified paraffin oil	8	3.3	1.5	1.3	1	1

b) SC formulation. Table 8

ADJUVANT appln. rate 1 Kg/ha	INFECTION SCORE a.i. application rate, g/ha					
	0	12.5	25	50	100	200
none	7.8	6.3	3.5	3.5	3.3	3.3
ARKOPAL N-060	7.8	2.5	1.3	1	0.5	0.3
ARKOPAL N-100	8.8	2.3	1.3	1	0.8	0.8
ARKOPAL N-230	8.5	3.8	2.3	2	1	1.3
emulsified paraffin oil	6.5	3	0.8	1.5	0.5	0.8

Trial 3 - Effect of adjuvants on the therapeutic control of 1 day old infections of powdery mildew on wheat

a) EC formulation. Table 9

GENAPOL C-080 appln. rate g/ha	% LEAF AREA SPORULATING LESIONS a.i. application rate, g/ha					
	0	6.3	12.5	25	50	100
0	80	43	33	15	4	2
187	70	23	10	1	0	0
375	65	15	7	2	0	0
750	58	11	7	1	0	0
1500	55	11	6	0	0	0

b) SC formulation. Table 10

GENAPOL C-080 appln. rate g/ha	% LEAF AREA SPORULATED LESIONS a.i. application rate, g/ha					
	0	6.3	12.5	25	.50	100
0	83	68	40	35	25	38
187	73	15	5	3	1	0
375	55	12	5	2	0	0
750	55	14	2	1	0	0
1500	60	15	4	1	0	0

Trial 3 - Effect of adjuvants on the therapeutic control of 1 day old infections of septoria on wheat

a) EC formulation. Table 11

GENAPOL C-080 appln. rate g/ha	INFECTION SCORE a.i. application rate, g/ha					
	0	6.3	12.5	25	50	100
0	7.5	8	5	3	2	2
187	7	3.3	3	2	0.8	1.3
375	7.5	3	2.5	1.3	1.5	0.8
750	6.3	3.3	2.5	1.8	0.8	1.0
1500	6.3	2.5	2.3	2	1	1.5

b) SC formulation. Table 12

GENAPOL C-080 appln. rate g/ha	INFECTION SCORE a.i. application rate, g/ha					
	0	6.3	12.5	25	50	100
0	7	6.5	6.3	6.3	6.5	5.8
187	7	3.3	3	1.5	1	1.8
375	6.8	3.8	3	2	1.8	1.3
750	7.5	4.5	1.8	1.5	0.5	1
1500	4.8	1.5	1.3	1	0.5	0.5

Trial 4 - Effect of adjuvants on the therapeutic control of 1 day old infections of powdery mildew on wheat

EC formulation. Table 13

ADJUVANT	ADJUVANT appln. rate g/ha	% LEAF AREA SPORULATING LESIONS a.i. application rate, g/ha				
		0	6.3	12.5	25	50
none	-	80	38	16	6	3
GENAPOL C-080	250	-	13	6	2	0
	500	-	7	4	0	0
	1000	-	13	4	3	0
	1500	50	19	8	1	0
ARKOPAL N-100	250	-	15	6	4	2
	500	-	15	5	4	1
	1000	-	15	5	3	2
	1500	50	13	8	3	0
emulsified paraffin oil	250	-	38	5	1	0
	500	-	20	6	1	0
	1000	-	23	6	2	0
	1500	53	15	1	1	0

Trial 4 - Effect of adjuvants on the therapeutic control of 1 day old infections of septoria on wheat

EC formulation. Table 14

ADJUVANT	ADJUVANT appln. rate g/ha	INFECTION SCORE a.i. application rate, g/ha				
		0	6.3	12.5	25	50
none	-	7.3	6	3.3	1.5	0.5
GENAPOL C-080	250	-	1.8	1	0.5	0
	500	-	1.3	0.8	0.3	0
	1000	-	1.3	1	0	0.3
	1500	7	1.3	0.5	0.8	0.5
ARKOPAL N-100	250	-	5.3	2	1.3	0.8
	500	-	3.5	1.3	0.5	0.3
	1000	-	3	1.5	0.8	0.5
	1500	8	3.5	1.8	1	0.5
emulsified paraffin oil	250	-	3.5	1	0.5	0.5
	500	-	5	1	0.8	0.5
	1000	-	3.5	1.3	0.5	0.8
	1500	8	4.5	0.8	0.8	0.5

Trial 5 - Effect of adjuvants on the therapeutic control of 1 day old infections of powdery mildew on wheat

EC Formulation. Table 15

ADJUVANT appln. rate 500g/ha	INFECTION SCORE a.i. application rate, g/ha					
	0	6.3	12.5	25	50	MEAN*
none	8.2	7	5.5	3.5	2.5	4.6
DOBANOL 91-5	7	2	2	1.7	0.7	1.6
DOBANOL 91-8	7	4.2	1.7	0.6	0.1	1.7
DOBANOL 23-6.3	6.5	2.2	2.2	1.7	0.2	1.6
DOBANOL 25-7	7.5	3	1.7	0.5	0.5	1.4
DOBANOL 25-9	7	5	1.7	0.2	0.1	1.8
DOBANOL 45-7	6.5	1.7	2.2	1	0.4	1.3
GENAPOL C-050	7	2.5	1.7	0.6	0.4	1.3
GENAPOL C-080	7.5	3	2.5	0.6	0.5	1.7
emulsified paraffin oil	8	4.2	2.5	1.4	0.5	2.2
ATLAS G1281	7.5	4.2	3.5	3.7	1	3.1

* Mean value of all doses

Trial 6 - Effect of different DOBANOL adjuvants on the therapeutic control of 1 day old infections of powdery mildew on wheat

SC formulation. Table 16

ADJUVANT		INFECTION SCORE					
NAME	appln. rate g/ha	a.i. application rate, g/ha					
		0	6.3	12.5	25	50	MEAN*
none	-	8.8	8.5	8.5	9	9	
DOBANOL 91-8	250	-	6.5	4.5	1.5	1	2.6
	500	-	5.5	2	1.3	0	
	1000	-	5	2	1.3	0	
	1500	8	5.5	2	2	0	
DOBANOL 25-7	250	-	7	4.3	1.1	1.2	2.7
	500	-	7	4	0.1	0	
	1000	-	5.5	4.5	0.7	0	
	1500	8	3.5	2.5	0.1	0	
DOBANOL 45-7	250	-	6	4	0.8	0.3	1.9
	500	-	6	1.5	0.1	0	
	1000	-	4	0.8	0.1	0	
	1500	7.5	5.5	1.5	0.3	0.1	

* Over all a.i. concentrations and adjuvant application rates

Trial 7 - Effect of different adjuvants on the therapeutic control of 1 day old infections of powdery mildew on wheat

SC formulation. Table 17

ADJUVANT		INFECTION SCORE				
NAME	appln. rate g/ha	a.i. application rate, g/ha				
		0	6.3	12.5	25	50
none	-	9 (0)	9 (0)	8.6 (0.5)	8.6 (0.5)	8.8 (0.3)
DOBANOL 91-6	250	-	7.8 (0.5)	7.3 (0.9)	5.9 (0.9)	3 (0)
DOBANOL 91-6	500	-	5.9 (0.6)	4 (2.4)	1 (0.3)	0.3 (0.2)
DOBANOL 91.6	750	8.8 (0.3)	6 (1.2)	2.9 (2)	0.4 (0.2)	0.1 (0.1)
DOBANOL 91-8	250	-	7.4 (0.5)	5.5 (1)	2.6 (1.1)	1.1 (1.8)
DOBANOL 91-8	500	-	7.4 (0.9)	3.8 (1.5)	1.8 (1)	0 (0)
DOBANOL 91-8	750	9 (0)	7.5 (0.6)	3.5 (0.6)	1.1 (0.7)	0.1 (0)
DOBANOL 23-63	250	-	6.5 (0.6)	4.5 (0.6)	5.3 (1)	2.6 (0.9)
DOBANOL 23-63	500	-	6.8 (0.5)	3.6 (1.5)	0.6 (0.3)	0.5 (0.4)
DOBANOL 23-63	750	8.9 (0.3)	6.9 (1.0)	3.8 (1.5)	0.9 (0.2)	0.1 (0.1)
DOBANOL 45-7	250	-	7.5 (0.4)	4.8 (0.5)	1.8 (1)	0.3 (0.2)
DOBANOL 45-7	500	-	5.9 (1.3)	3.8 (1.3)	0.6 (0.3)	0.1 (0.1)
DOBANOL 45-7	750	8.9 (0.3)	7.3 (0.3)	5.5 (1.7)	1.1 (0.6)	0.1 (0.1)
GENAPOL O-050	250	-	8.6 (0.5)	8.4 (0.6)	7.5 (0.6)	7 (0)
GENAPOL O-050	500	-	8.8 (0.3)	8 (0)	7 (0.8)	5 (0.2)
GENAPOL O-050	750	9 (0)	8.8 (0.3)	7.8 (0.3)	6.8 (1.3	3 (0.8)

( ) - standard deviations

N.B. In this trial results are the means of four replicate pots of plants.

Example Set 2

a) Materials

A suspension concentrate (SC) was prepared, corresponding to that described above in Example Set 1. An emulsifiable concentrate (EC) similar to that described above in Example Set 1, was prepared, having the following composition.

Emulsifiable Concentrate

a.i.		100 g
TENSIOFIX NS		64 g
TENSIOFIX GS		16 g
SURFADONE LP100		70 g
N-butanol		40 g
SHELLSOL A	to	1 l.

In each case the active ingredient consisted essentially of the "cis" isomers, as used for Trials 6 to 7 of Example Set 1.

The SC and EC formulations used in Example Set 2 were used as such, for comparison purposes, and were mixed with adjuvants including alcohol ethoxylates. In some cases, the SC or EC formulation, and the adjuvant(s), were separately added to water in a spray tank to form "tank-mix" formulations. In other cases the SC or EC formulation and the adjuvant(s) were mixed together to form pre-mixed "one-pack" formulations, to be added to water in a spray tank.

"One pack" soluble liquid (SL) compositions were prepared, having the following compositions:

Ingredient	SL (1)	SL (2)	SL (3)	SL (4)
a.i.	100	80	60	40
DOBANOL 91-6	-	600	600	600
DOBANOL 23-6.5	500	-	-	-
NMP *	300	-	-	-
amyl alcohol	to 1l.	to 1l.	to 1l.	to 1l.

* NMP: N-methyl pyrrolidone

In other, comparative SL compositions, the DOBANOL adjuvants were replaced with other adjuvants.

Most of the adjuvants used have already been described in Example Set 1. Other adjuvants described in this Example Set 2 are:

- corn oil emulsifiable concentrate
- ARMOBLEN 557, an alkylamine ethoxylate/propoxylate, from Akzo.

Further "tank-mix" formulations were prepared by adding a second active ingredient to "tank-mix" formulations containing the SC composition described above and an alcohol ethoxylate adjuvant. The second active ingredients were dithianon (available from Shell under the Trade Mark DELAN), fenpropimorph (available from B.A.S.F. under the Trade Mark CORBEL) and chlorothalonil (available from B.A.S.F. under the Trade Mark BRAVO).

b) Plants

Winter wheat seeds, cv Hornet, were sown in 7 cm square pots. This resulted in establishment of 20 to 25 plants per pot. After 12 days, under normal glasshouse conditions as described above, by which time the seedlings were at the 1-2 leaf stage, the plants were inoculated with Erysiphe graminis fsp tritici from a stock infection. Treatments were applied on day 13, usually about 28 hours after inoculation. Plants were then laid out in a controlled environment compartment of a greenhouse using a randomised double-block design to reduce variation due to placement. Watering was carried out by means of an automated sub-irrigation matting system.

c) Preparation and application of spray solutions

All test solutions were sprayed at four doses, the difference between doses being a factor of x2, usually 12.5, 25, 50 and 100 g/ha of a.i.. A single quantity of each product was weighed out for all of the doses of that product. When adjuvant was added as a single a.i. : adjuvant ratio, the whole batch was prepared for the highest dose, then appropriate aliquots diluted with tap water to the correct concentrations for the lower doses. When adjuvant was added at a single dose per hectare for all treatments, the base formulation was made up at double the required concentration and then each dose diluted to the correct concentration using a stock solution of the adjuvant. All applications were made using a moving track sprayer fitted with a single flat-fan nozzle calibrated to give 400 l/ha of spray. Four pots (replicates) were sprayed with each treatment.

d) Assessment

Estimates of infection were made, in some cases after about one week, then after about two weeks if the results were of further interest. Usually the initial assessment was a score on a 0 to 9 scale, where 0 = no infection and 9 = very high infection of inoculated leaves. Later assessments were usually of percentage of leaf area infected by the mildew.

e) Results

The results are presented in graphical form in the following pages and information particular to the particular test is presented above the appropriate graph.

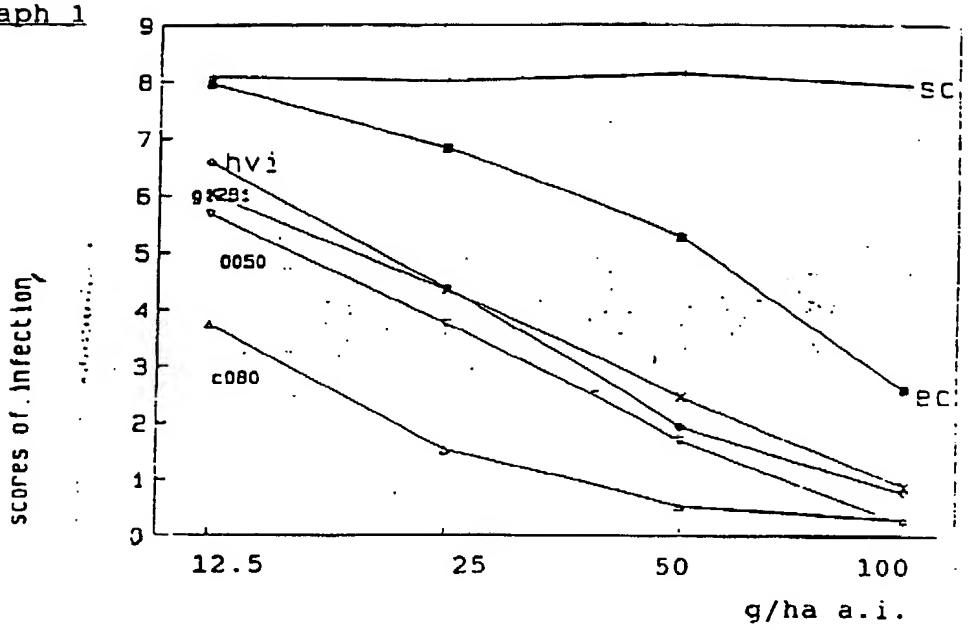
(i) Example Set 2, Results 1

Graph 1 below presents the mean results of three series of tests intended to test the comparative efficacies of the adjuvants GENAPOL 0-050, GENAPOL C-080, ATLAS G1281, and HVI 60 paraffinic oil containing 100 g/l EMULSOGEN M. The SC and EC lines relate to the efficacy of spray compositions derived from the SC and EC formulations described above, without adjuvants.

The first series of tests employed a "tank-mix" with the SC. The second series of tests employed a "tank-mix" with the EC. The third series of tests employed "one-pack" formulations. In each case the adjuvant : active ingredient ratio was 10 : 1 (w : w).

Assessment was made 7 days after treatment.

Graph 1



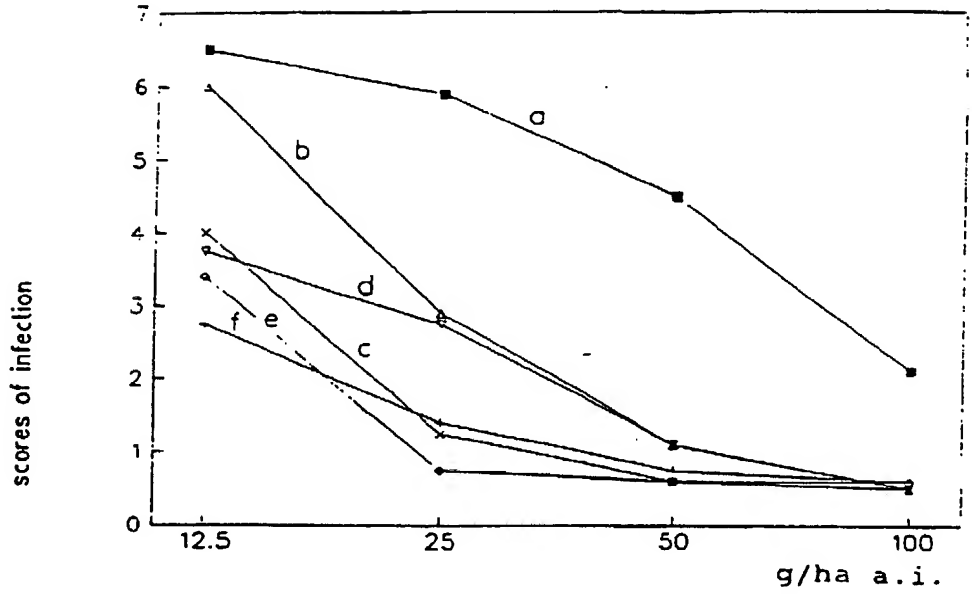
(ii) Example Set 2, Results 2

Graph 2 below presents the mean results of a series of tests showing the comparative efficacies of various adjuvants. The spray compositions were derived from "one-pack" formulations, coded as follows:

a - EC described above
b - EC containing corn oil adjuvant
c - EC containing HVI 60
d - EC containing ARMOBLEN 557
e - SL containing DOBANOL 91-6
f - SL containing GENAPOL C-080.

In each case the adjuvant : active ingredient ratio was 10 : 1 (w : w)
Assessement was made 7 days after treatment.

Graph 2

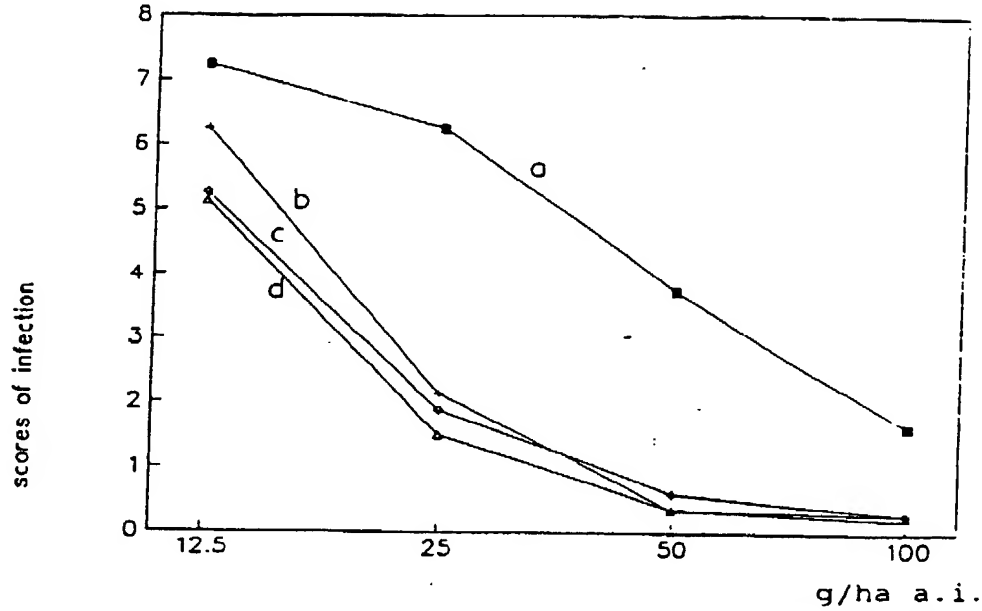


(iii) Example Set 2, Results 3

Graphs 3(a) and 3(b) below present the mean results of a series of tests intended to test the efficacy of HVI-60 paraffinic oil adjuvant and DOBANOL 91-6 alcohol ethoxylate adjuvant over a range of active ingredient and adjuvant application rates. The formulations to be diluted for spraying were prepared as "one-pack" formulations, the HVI-60 with the EC formulation, and the DOBANOL 91-6 with the SL formulation.

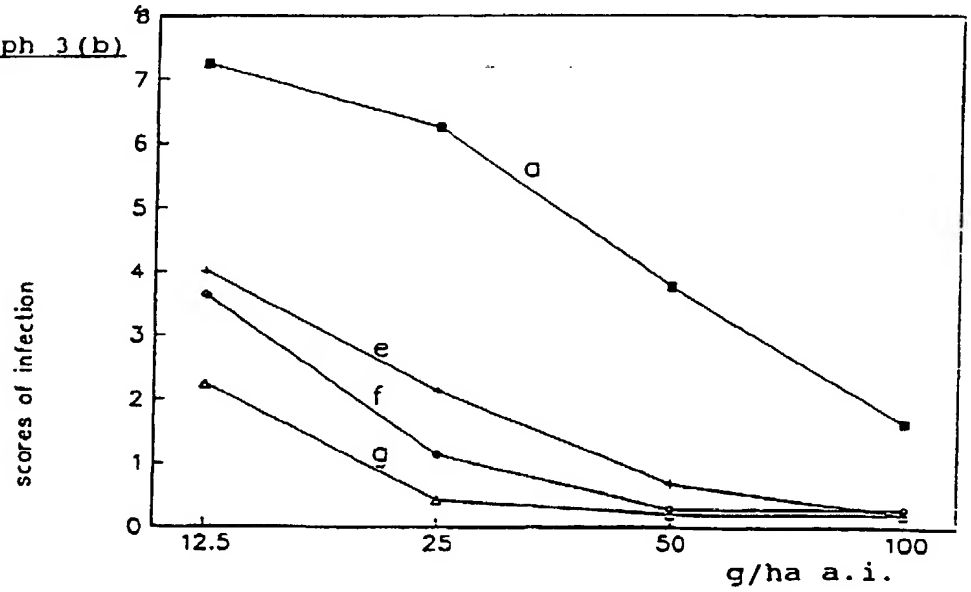
Assessment was made 7 days after treatment.

Graph 3(a)



a = EC, b = 5:1, c = 10:1, d = 20:1 EC compositions
(HVI : a.i. - w : w)

Graph 3(b)



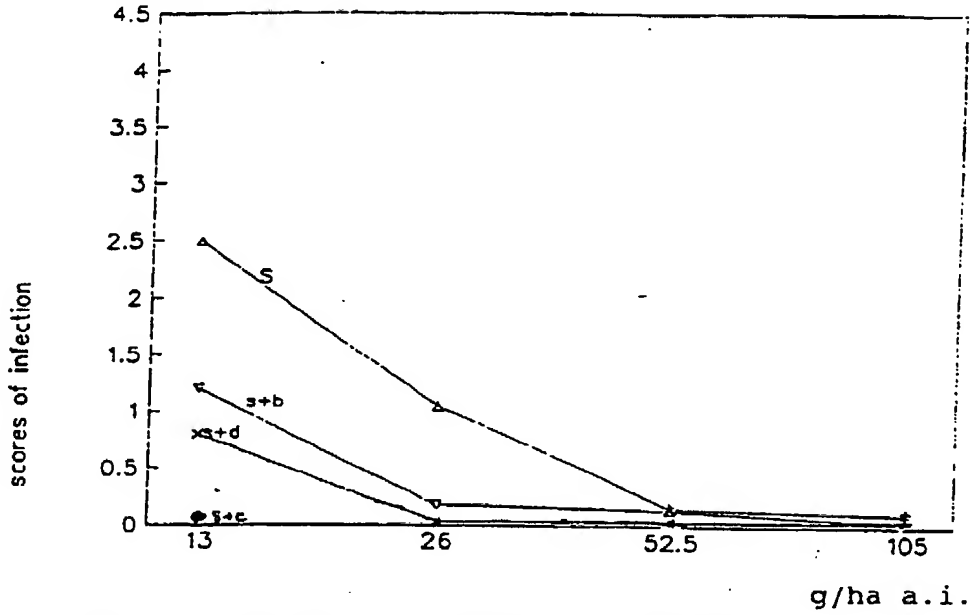
a = EC, e = 5:1, f = 10:1, g = 20:1 SL compositions
(DOBANOL : a.i. (w : w)

(iv) Example Set 2, Results 4

Graphs 4(a) and 4(b) below present the mean results, 7 days after treatment and 14 days after treatment, respectively, following testing of various "tank-mix" compositions, employing the SL formulations with an ad-

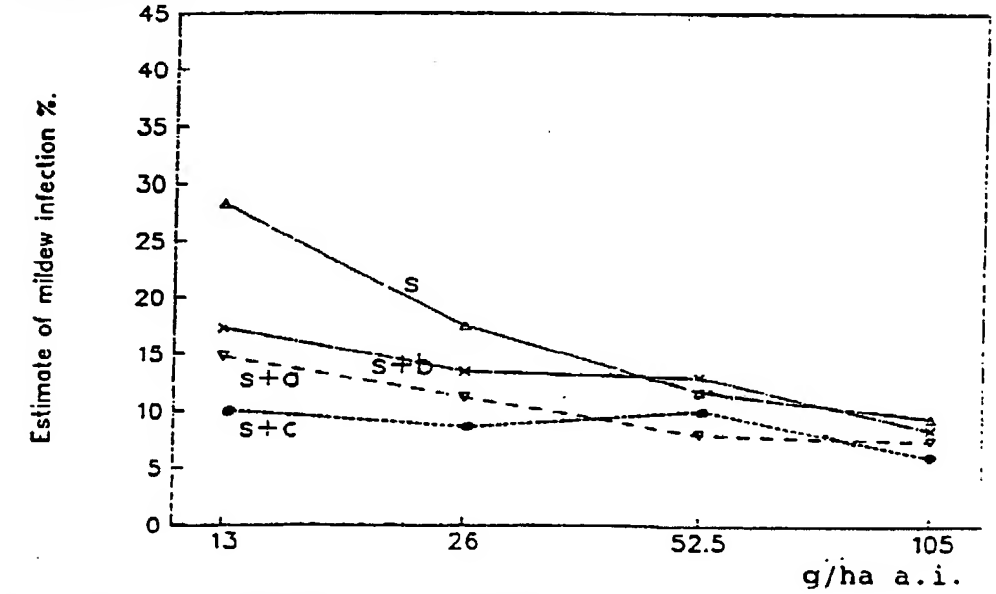
juvant : a.i. ratio of 10 : 1 (w : w).

Graph 4(a)



S = SL, d = DELAN, b = BRAVO, c = CORBEL.
S + c is near 0 throughout.

Graph 4(b)

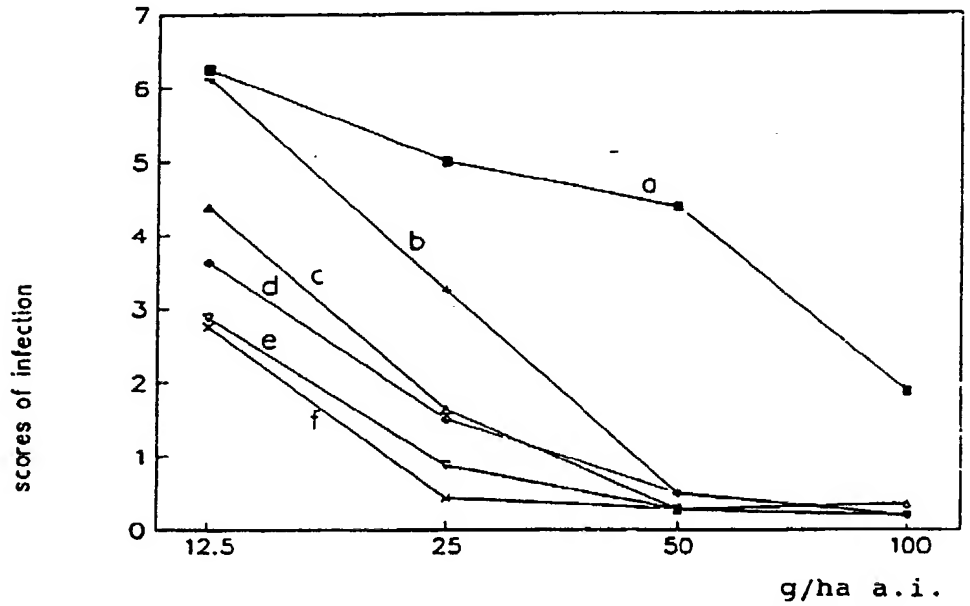


S = SL, c = CORBEL, b = BRAVO, d = DELAN

(v) Example Set 2, Results 5

Graph 5 below presents the mean results, 7 days after treatment, of testing various spray compositions, with different a.i. and adjuvant application rates, derived from "one-pack" SL formulations of DOBANOL 91-6. Assessment was made 7 days after treatment.

Graph 5



a = EC, b = 5:1, c = 10:1, d = 7.5:1, e = 20:1, f = 15:1,

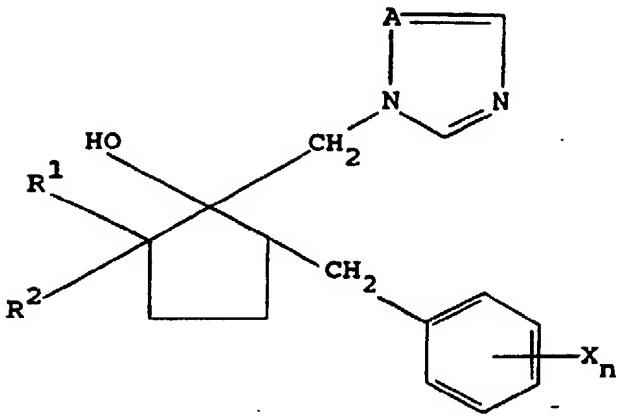
SC compositions (DOBANOL 91-6 : a.i. - w : w)

It should be noted that the use of capital letters in this specification to denote terms for materials indicates that those terms are, or are thought to be, trade marks.

It should be noted that the information which has been provided about the chemical constitution of the various materials designated by trade marks has been provided on the basis of common knowledge, and, where available, manufacturers' or distributors' information.

Claims

1. A fungicidal composition which comprises a compound of general formula:



(I)

or acid addition salts or metal complexes thereof, wherein R^1 and R^2 each independently represents a C_{1-6} alkyl group or a hydrogen atom; X represents a halogen atom, a C_{1-6} alkyl group or a phenyl group; n is 0, 1 or 2 and A represents a nitrogen atom or CH; and an alkoxylate of an aliphatic alcohol.

2. A composition as claimed in claim 1, wherein the alkoxylate comprises 5 to 25 alkoxy moieties.

3. A composition as claimed in claim 2, wherein the alkoxylate comprises 5 to 9 alkoxy moieties.

4. A composition as claimed in any preceding claim, wherein the alkoxylate is an ethoxylate or a mixed ethoxylate/propoxylate.

5. A composition as claimed in any preceding claim, wherein the aliphatic alcohol is a C_{9-18} aliphatic alcohol.

6. A composition as claimed in any preceding claim, wherein a) the alcohol moiety is a primary alcohol moiety or, when there is a mixture of alcohol moieties, they are predominantly primary; b) the alcohol moiety is straight-chain or, when there is a mixture of alcohol moieties, they are predominantly straight-chain; c) the alcohol moiety has only one hydroxy group or, when there is a mixture of alcohol moieties, alcohol moieties with only one hydroxy group predominate; or d) the alcohol moiety is saturated or, when there is a mixture of alcohol moieties, saturated alcohol moieties predominate.

7. A composition as claimed in any one of the preceding claims, further comprising a compound selected from dithianon, chlorothalonil and fenpropimorph.

8. A composition as claimed in any one of the preceding claims, wherein R^1 and R^2 both represent a methyl group, A represents a nitrogen atom and X_n represents a 4-chloro atom.

9. A composition as claimed in claim 8, wherein the active ingredient consists of or predominantly comprises isomers in which the hydroxy and the halobenzyl moieties are arranged "cis" to each other.

10. A fungicidal composition as claimed in any one of the preceding claims, being a concentrate formulation for addition to water, and containing in the range of from 5 to 200 g/kg of a compound of general formula I, and in the range of from 100 to 500 g/kg of an alkoxylate of an aliphatic alcohol.

11. A method of combating a fungus at a locus, which method comprises treating the locus with a composition which contains a compound of general formula I, as defined in claim 1, and an alkoxylate of an aliphatic alcohol.

12. A method as claimed in claim 15, wherein a compound of general formula I is applied to the locus in an amount in the range of from 50 to 300 g/ha, and the alkoxylate, in an amount in the range of from 300 to 1500 g/ha.

13. Use as a fungicide of a composition as claimed in any of claims 1 to 10.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 92 30 6960

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 158 374 (JANSSEN PHARMACEUTICA) * page 5, line 18 - line 19 * * page 7, line 30 - line 35 *	1-13	A01N43/653 A01N43/50
D,Y	GB-A-2 180 236 (KUREGA KAGAKU KOGYO) * page 15, line 14 - line 21 *	1-13	
Y	FR-A-2 588 724 (RHONE-POULENC AGR.) * page 1, line 24 - line 25 * * page 1, line 30 - line 35 * * claims *	1-13	
D,Y	EP-A-0 267 778 (KUREGA KAGAKU KOGYO) * page 42, line 19 - line 23 *	1-13	
A	EP-A-0 394 847 (BASF)		
D,A	EP-A-0 357 404 (KUREA KAGAKU KOGYO)		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

A01N

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 NOVEMBER 1992	DALKAFOUKI A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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